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Adsorption of hydrogen peroxide on the surface of silica – titania mixed oxide obtained by the sol-gel processing method

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Abstract: This work describes the sol-gel mixed oxide SiO₂/TiO₂ property, ST, as prepared, and submitted to heat treatment at 773 K, STC. SEM and EDS images show, within magnification used, a uniform distribution of the TiO₂ particles in SiO₂/TiO₂ matrix. Both, ST and STC adsorb hydrogen peroxide on the surface and through EPR and UV-Vis diffuse reflectance spectra, it was possible to conclude that the species on the surface is the peroxide molecule attached to the Lewis acid site of titanium particle surface, α -Ti(H₂O₂)⁺. As the material is very porous, presumably the hydrogen peroxide molecule is confined in the matrix pores on the surface, a reason why the adsorbed species presents an exceptional long lived stability.

Keywords: sol-gel; silica-titania; hydrogen peroxide adsorption; porous material.

Introduction

The sol-gel process can be described as a very convenient method to prepare binary oxides such as SiO₂/M_xO_y, with high purity and homogeneity [1-6]. Among these, SiO₂/TiO₂ having high concentration of titanium (IV) homogeneously dispersed in the matrix can be obtained by this process [7]. The metal oxide incorporated in the matrix is coordinatively unsaturated and furthermore can react with other compounds, resulting in an immobilized solid system [8]. As an example, the reactive α -TiOH groups on the SiO₂/TiO₂ surface can react with hydrogen peroxide, resulting in the solid SiO₂/TiO₂/H₂O₂ where the hydrogen peroxide group is adsorbed.

Several works dealing with the interaction of H₂O₂ with TiO₂ have been reported, emphasizing the importance of the mechanism of this reaction in biochemical and chemical processes [9-10]. The structure of the adsorbed species has also been investigated, but the mechanism of the radical formation is still not well understood [11-14].

Hydrogen peroxide chemisorbed on titanium dioxide, hereafter named peroxide-modified titanium dioxide, is investigated as a chemical

analog to the putative soil oxidants responsible for the chemical reactivity [15].

Supported oxide catalysts containing transition metal ions are known to be widely used in oxidation of organic substances with molecular oxygen. Therefore it seems interesting to study the state of the oxygen absorbed on their surface [16-19].

The EPR measurements [12, 19-20] have shown that the oxygen adsorption on n-semiconducting oxides and radiation chemisorptions on dielectrics results in formation of the O₂-adsorbed radicals. This technique has been widely used for the studies of supported oxide catalysts.

It has also been shown that metallic titanium and hydrogen peroxide interacts strongly and that a titanium-peroxide gel with pH around 4 are formed, then has been showed that hydrogen peroxide decomposed [21-22].

The presence of such radicals may be of considerable importance in many research areas, such as photochemistry, solar energy conversion

[9, 23-25], and the biochemistry of respiration and inflammation [10-11].

This work reports the interaction of hydrogen peroxide (H_2O_2) on the surface of silica-titania (SiO_2/TiO_2) mixed oxide obtained by the sol-gel processing method. Studies have shown that H_2O_2 would form stable peroxide radicals adduct with SiO_2/TiO_2 . In this study, adsorption of H_2O_2 by SiO_2/TiO_2 from aqueous solutions is investigated as well as the formation of peroxide radicals by Electron Paramagnetic Resonance (EPR) and visible-UV spectrometry using a diffuse reflectance technique.

Experimental details

Preparations

SiO_2/TiO_2 mixed oxide was prepared by the sol-gel processing method as described elsewhere [26], (1) 12.1 mL of 0.85 mol.L⁻¹ HNO_3 aqueous solution were added to 250 mL of 50% (v/v) tetraethoxysilane (TEOS)/ethanol solution, and the mixture was stirred at 353 K for 2.5 h. (2) About 34 mL of titanium (IV) butoxyde (TBO) and 490 ml of ethanol were then added and the mixture was stirred for 2 h at room temperature. (3) 66 ml of 0.6 mol.L⁻¹ HNO_3 solution were slowly added and allowed to rest for gelation. The formed xerogels were ground, dried at 383 K for 24 h and sieved in order to obtain particles size between 75 and 250 μm .

Parts of SiO_2/TiO_2 samples were calcined at 773 K under air flux. The untreated and heat-treated silica-titania samples were designated as ST and STC, respectively. The solid was analyzed by using the X-ray fluorescence technique on a Tracor Northern X-ray fluorimeter.

Adsorption of the hydrogen peroxide on SiO_2/TiO_2

About 10 g SiO_2/TiO_2 (calcined, STC and uncalcined, ST) samples were shaken for 30 min with 100 mL of 0.5 mol.L⁻¹ hydrogen peroxide solution. The solutions were decanted and the hydrogen peroxide determined by iodometric titration in the solution phase. The solid was submitted to high vacuum for 30 min at 298 K.

Uv-VIS Spectroscopy

Uv-Vis electronic spectrum of the materials SiO_2/TiO_2 and $SiO_2/TiO_2/H_2O_2$ they were

obtained by diffuse reflectance technique. The spectra were obtained in the region between 200 and 800 nm, at ambient temperature, using a UV-Vis-NIR Variam Cary 5G spectrophotometer connected to a diffuse reflectance accessory using $BaSO_4$ as reference.

Electron Paramagnetic Resonance

The spectra were been obtained in a X-band frequencies on a Bruker ESP 300E spectrometer, operating in X band (9.77 GHz). Room temperature measurements were obtained with frequency modulation of 100 kHz and amplitude modulation of 15.7 G. The measures had been obtained in the temperature of liquid nitrogen with microwave frequency of 9.46GHz and microwave power of 2×10^{-1} mW. The field sweep width was 798 G with acquisition time of 671 s. The g value is referenced to the one of DPPH.

Results and Discussion

Table 1 shows the results of the titanium analyses in the binary oxide, ST and STC, the results on specific surface areas and average pores volume. For the mixed oxide SiO_2/TiO_2 , designated as ST, the measurements were made as prepared and, for mixed oxide designated as STC, the measurements were made after heat treatment at 773 K.

Table 1: Chemical titanium analysis in oxides binary, Specific Superficial Area, S_{BET} , and average volume of the pores, V_p .

Matrix	Ti/wt%	$S_{BET}/m^2 g^{-1}$	$V_p/mL g^{-1}$
ST	26,4	573	0,29
STC	28,0	468	0,31

The results of specific surface area S_{BET} (Table 1) show that for STC a reduction of the area after is observed under thermal treatment as consequence of pores collapse [26-28]. However, the observed area decrease is very small indicating that TiO_2 particles inside the SiO_2 matrix is thermally few mobile upon treatment at this temperature. As consequence, the average pore volume remains practically the same after the heat treatment.

The materials submitted to the scanning electron microscopy ST and STC have shown that the titanium is distributed uniformly on the material,

as can be observed by Figure 1. The thermal treatment of STC (calcination at 773 K under air flow) did not modify the uniform distribution of titanium oxide particles in the material. Within the magnification used, this fact demonstrates that not formation of any islands in the mixed oxide [26]. Analysis by X-ray diffraction have shown that the materials are amorphous and thermally very stable [26].

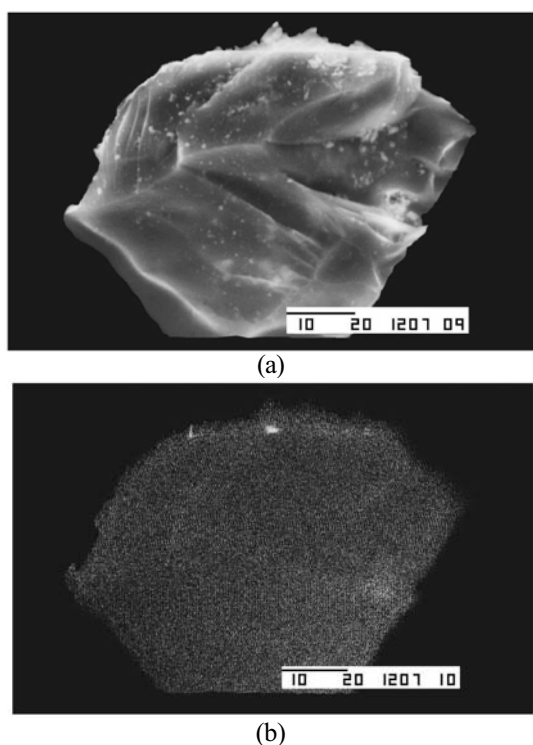
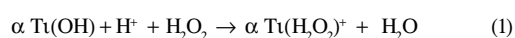


Figure 1: (a) Scanning electron micrographs of ST and (b) the corresponding EDS image for Ti atoms.

In solutions of low pH surface Ti(IV) reacts with H_2O_2 with the formation of a complex of yellow coloration (reaction 1). This property has been used as procedure of analytical chemistry to determine this metallic ion [29-30]. In this case after the immersion of binary oxides ST and STC in a H_2O_2 solution, the solid became yellow due to the formation of the complex on the surface of the material.

The reaction that occurs on the surface can be represented by the following equation:



where $\alpha \text{ Ti(OH)}$ is the hydroxyl group attached to titanium on the surface of the matrix and $\alpha \text{ Ti(H}_2\text{O}_2)^+$ represents the complex titanium-peroxide formed on the surface of binary oxide.

The UV-vis spectrophotometry was used to check the formation of the hydrogen peroxide complex on the matrix. Figure 2 shows the electronic spectra ST and ST/ H_2O_2 . It shows the LM charge transfer oxygen to the metal, for ST, at 352 nm. After treatment and adsorption of peroxide on the surface, LM is observed at 400 nm for ST/ H_2O_2 , a clear indication that on the surface the titanol group ($\alpha \text{ Ti(OH)}$), was replaced by hydrogen peroxide molecule $\alpha \text{ Ti(H}_2\text{O}_2)^+$ [31-33].

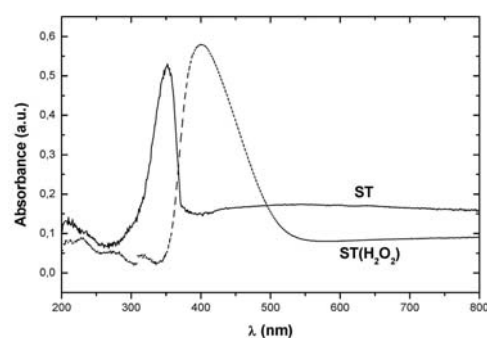


Figure 2: Uv-Vis electronic spectrum of diffuse reflectance of ST and ST(H_2O_2).

Electron paramagnetic resonance spectrum for STC/ H_2O_2 (Figure 3), shows three values for g: 2.00, 2.01 and 2.03. These values are assigned to superoxide species on the matrix surface [34].

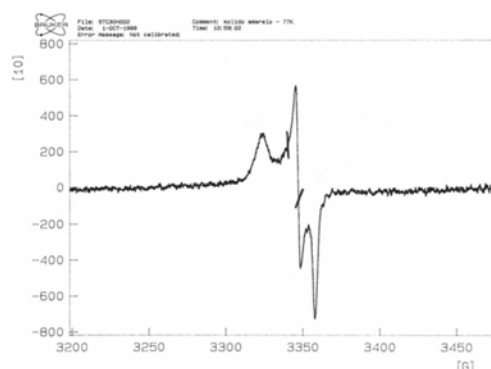


Figure 3: EPR spectrum of the material STC/ H_2O_2 . The data were obtained at 77 K.

Isotherm of adsorption

In order to determine the matrix adsorption capacity of hydrogen peroxide, the isotherm of adsorption at 298 K was determined. Figure 4 shows the isotherms obtained for STC for solid immersed in a solution containing the solid at pH 3. Saturation of the STC surface by H_2O_2 is achieved for surface concentration of peroxide of 0.9 mmol.g^{-1} at pH 4. This adsorption of hydrogen peroxide on the surface may occur exclusively on the Lewis acid sites.

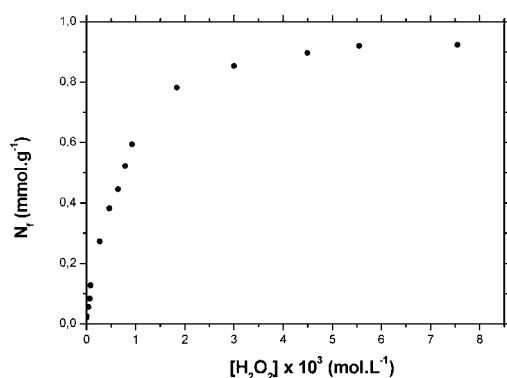
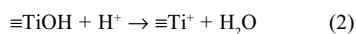


Figure 4: Isotherm of adsorption of hydrogen peroxide on STC matrix at 298 K and pH 3.

The effectiveness in adsorbing H_2O_2 by the material as prepared, ST, and submitted to calcination, STC, for a fixed concentration of peroxide and using nearly the same mass of ST or STC, was tested by determining the amount of H_2O_2 adsorbed at various pH. Figure 5 shows that for both matrices, at various solutions pH, the adsorption capacities determined are nearly the same. The maximum adsorption occurred at pH between 3 and 4. A supposition that Lewis acid sites are the reactive centers and they are generated at lower pH by the reaction is clearly supported by this experiment [31]. The reaction which occurs can be represented by the reaction 2:



When pH is much lower, *i.e.* below 3, it is presumed that an increase of anionic counter ion of the acid, used to adjust the solution pH, compete with peroxide at the solid-solution interface or, peroxide molecules are protonated at

this pH, decreasing the amount of this species on the surface.

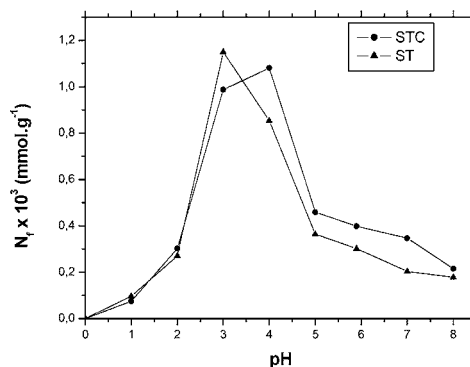


Figure 5: Isotherm of adsorption of hydrogen peroxide on ST and STC at various solutions pH. $[H_2O_2] = 1 \times 10^{-2} \text{ mol.l}^{-1}$, mass of 0.1 g for ST and STC used and temperature of 298 K.

Stability of adsorbed peroxide

Stability of adsorbed peroxide on ST and STC, was tested for ST/ H_2O_2 and STC/ H_2O_2 heated at 333 K. In this case, for both materials, an approximate 5 wt% reduction of peroxide adsorbed was detected. After longer time allowed to rest at room temperature, about nine months, a loss of 50 wt% of hydrogen peroxide was observed. A complete and fast decomposition of peroxide is observed when the samples, ST(H_2O_2) and STC(H_2O_2), are heated at 373 K for 45 min. This experiment shows how the peroxide molecule adsorbed in the pores of ST and STC matrices are stabilized.

Regeneration of the matrix

As the ST and STC is a matrix where the silica framework confers an exceptional mechanical and chemical stability to the TiO_2 particles, linked to matrix by Si-O-Ti bond, after treatment with hydrogen peroxide it is not leached to the solution phase. A complete regeneration of the matrix is possible heating the sample at 373 K during 45 min for a complete regeneration of the matrices ST(H_2O_2) and STC(H_2O_2) and prompt to be reused.

Conclusions

The mixed oxide SiO_2/TiO_2 , prepared by the sol-gel processing method, as prepared (ST) and submitted to heat treatment (STC) showed that the matrix obtained is very resistant under

mechanically and chemically point of view. The low thermal mobility of TiO₂ particles and the resistance of silica framework, resulted only in a small S_{BET} decrease of STC in comparison with ST. The scanning electronic microscopy showed that the titanium is uniformly distributed throughout the matrix.

The exceptional stability of H₂O₂, presumably confined in the pores of the matrix surface, as a•Ti(H₂O₂)⁺ species, under application point of view, represents as a new and attractive material useful as powerful oxidant in a chemical reaction under dynamical flow condition.

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